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Technical Report No. 32-15

Photographic Studies of the Combustion Characteristics of Metal Particles

Derck A. Gordon

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JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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ABSTRACT

An investigation of the combustion characteristics of particles of a number of metals, metallic compounds, and other substances has been made; the most important factors controlling the rate and completeness of combustion are listed. This information can be used to develop a theoretical basis for the selection of metals or the formulation of alloys having desirable burning characteristics – as well as other physical and chemical properties – to be used as additives to solid propellants for the purpose of increasing performance. The investigation has already led to the recommendation of one such alloy system; namely, the alloys of aluminum and magnesium.

I. INTRODUCTION

Finely divided metals or certain of their compounds and alloys are incorporated into solid propellants to suppress resonant burning phenomena, to modify other burning characteristics, and also to increase performance (Ref. 1). Although the mechanism by which particles of metal or other substances affect resonant and other burning characteristics of propellants is not well understood, these phenomena may be intimately associated with the kinetics of combustion in the gas phase and with the physics of the propagation of sound in an inhomogeneous, reacting medium. It is known that the increase in performance realized from the use of metal additives results from an increase in the combustion heat of the propellant and from a decrease of the mean molecular weight of the exhaust gases due to the removal of oxygen from CO_2 and H_2O. It therefore seems that the effect of metal particles in the capacity of performance-increasing additives can be understood mainly by focusing attention on the heat transfer and chemical reactions which take place inside a particle as well as at the interface of the particle and in the hot gases surrounding it.

The general requirements of a metal additive are that it have a large oxidation heat and a rapid burning rate. Secondary requirements, however, seriously limit the choice of metals and alloys which may be considered for incorporation in solid propellants; these requirements are summarized in the following paragraphs.

1. The particles must not be smaller than about one micron because of (a) the hazard of dust explosions and pyrophoricity, (b) the high percentage of oxide represented by a thin layer of oxide on a particle, (c) the tendency of small particles to act as thickening agents which make propellant compositions unmanageable, and

(d) the high cost, generally, of producing small particle sizes. (Some substances such as boron, however, are commercially available as submicron particles.)

2. The additives should not react with other propellant constituants during mixing, curing, or storage. The alkali metals and the heavier alkaline earth metals, their hydrides, and their alloys are not compatible with today's solid propellant compositions.

3. Particles should be equiaxed in shape rather than flake-like. Although flake-like particles would appear to be more desirable than spherical particles of the same mass because their greater surface-to-mass ratio affords faster, more complete burning and because their thin cross section permits more rapid heating to ignition temperature, in practice these particles are avoided because they act as thickening agents in propellant mixtures.

4. The additives should be non-hazardous and available in large quantities at low cost. Beryllium metal is toxic, costly, and there are only small supplies available (Ref. 2, 3). Zirconium-metal powder, particularly when moist, may explode spontaneously (Ref. 4). Mechanically-tough or high-melting alloys are difficult to pulverize by grinding or by atomization, and the production of particles of the desired size is consequently expensive.

5. The metal should have a high density in order to afford propellant compositions of correspondingly high density-impulse value. Heat of combustion per unit volume is suggested as a tentative rating of different metals and several metals are compared on this basis in Table 1. This method of rating is by no means generally valid because many other physical and chemical factors enter the calculation of the maximum I_{sp} for a given propellant system. Incidentally, it may be noted that for a composite solid propellant the additive concentration giving the maximum I_{sp} may correspond to a mixture having undesirable mechanical properties because of an insufficiency of binder.

6. The additives should not be such powerful positive or negative burning-rate catalysts that their effects cannot be corrected by small changes in formulation of the propellant.

As a result of these limitations, there is considerable need for research in order to understand the factors determining the burning rate of metal and alloy particles. With the aid of such information it is possible to formulate alloys having not only a high combustion heat and a high burning rate under the conditions encountered in a motor chamber but having also a maximum number of other desirable properties such as low chemical reactivity with the propellant and the brittleness or low melting

Table 1. Heats of oxidation per unit volume.

ELEMENT	M.P.*	B.P.*	OXIDE	M.P.*	B.P.*	HEAT OF OXIDATION KCal/cm³ (25°C)
B	2300°C	2550°C	B_2O_3	450°C	2250°C	33
Be	1278	2970	BeO	2550	4000	30
Ti	1725	>3000	TiO_2	1860	2930 dec	21
Al	660	2057	Al_2O_3	2030	3500	20
Zr	1830	>3000	ZrO_2	2690	4300	18
Si	1420	2355	SiO_2	1700	2000 dec	18
Mg	651	1107	MgO	2800	3080	10
Ce	848	1740	CeO	2600	3330	6
Li	186	1326	Li_2O	1730	2330	5
Na	98	880	Na_2O	1770 dec	920	2

*References 11, 12, 13, 14 give widely varying values for these data

point which make pulverization by grinding or atomization inexpensive.

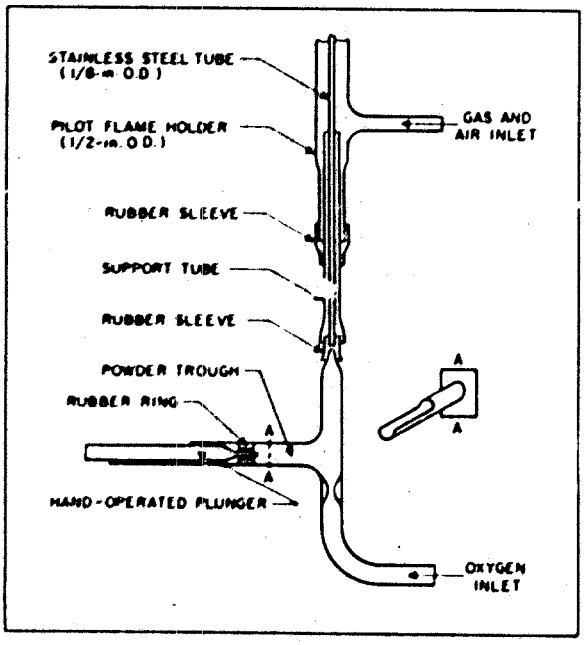
Considerable work has already been done in metal combustion and related fields: metal-dust explosions (Ref. 5), metal-oxygen torches (Ref. 6, 7), pyrotechnic mixtures (Ref. 8), thermite reduction (Goldschmidt Process) and oxidation of bulk metals at high temperatures (Ref. 9), and ignition temperatures of bulk metals (Ref. 10) have been studied. These studies did not appear promising as sources of information on the combustion of metal particles in solid propellants or on the basic mechanisms of particle combustion. With the exception of the studies on the oxidation rate of bulk metal, interpretation of observations in terms of basic principles and in terms of the physical and chemical properties of metals is, in general, impossible because of the many parameters involved. However, experiments with bulk metals would have excluded observation or phenomena associated with small particle size. Consequently, a new experimental method was sought which would permit observation of the effects of particle size, high heating rate and composition of the reacting atmosphere on the burning rate of metal particles, and which would give information readily interpretable in terms of basic combustion mechanics.

II. EXPERIMENTAL METHOD

A. The Particle-Burning Torch

The majority of the experiments were conducted with a *particle-burning torch*, an apparatus consisting essentially of a tube which conducts metal particles suspended in a stream of oxidizing or inert gas and ejects them into a gas-air pilot flame coaxial with the tube's exit (Fig. 1, 2). The pilot flame ignites the particles, which then burn in an atmosphere composed of the carrier gas and the combustion products of the pilot flame, the amounts of which can be varied at will. Early intentions were to study the effects of various carrier gases and to modify the pilot flame to give well-defined ignition conditions. However, experiments using oxygen as a carrier gas proved so fruitful that no essential changes or improvements were made.

The size of the pilot flame was varied as required by the ignitibility of the metal being tested and in order to study the effect of a hotter or less oxidizing atmosphere on the combustion of the particles. In the work described below, the pilot flame was generally adjusted to the minimum size which ignited the particles. This size



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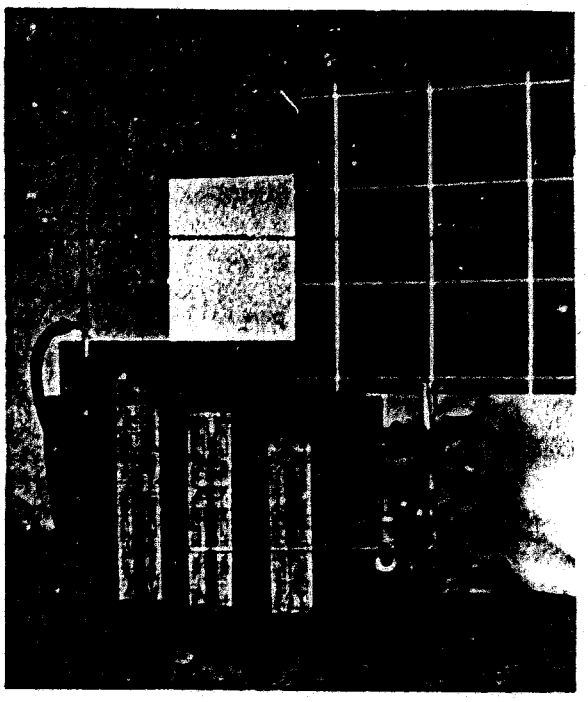

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varied from a low, open-top flame (Fig. 3) for magnesium and titanium (<325 mesh) to a high, closed-top flame (Fig. 4) for aluminum (<325 mesh).

The particle-burning torch was used principally to study isolated particles, but metal-oxygen flames could also be studied by increasing the concentration of metal injected into the oxygen carrier-stream. Metal-ogygen flames were created without damage to the torch because the flame did not attach itself to the nozzle, but was lifted several millimeters off the nozzle. However, radiation from large hot flames was often sufficient to heat the nozzle and cause it to burn away.

B. Observation and Recording

To record observations and to make quantitative measurements of burning time, burning particles were watched at close range or were photographed at various speeds with a still camera or with a moving picture camera; high-speed motion pictures at 1000 or more

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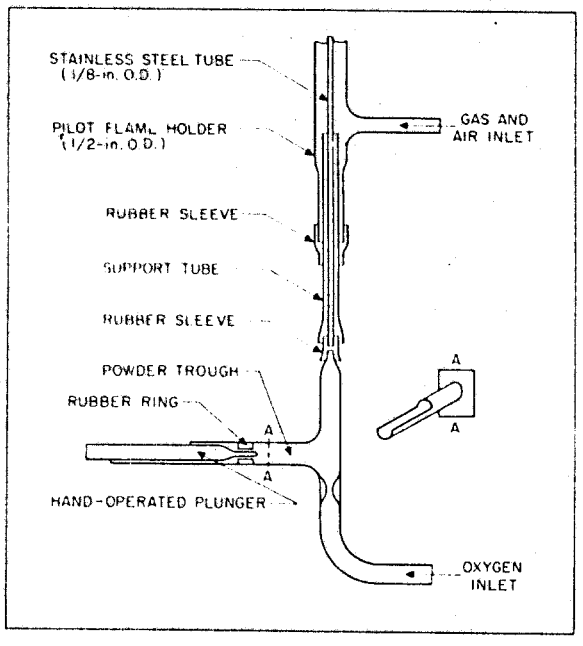

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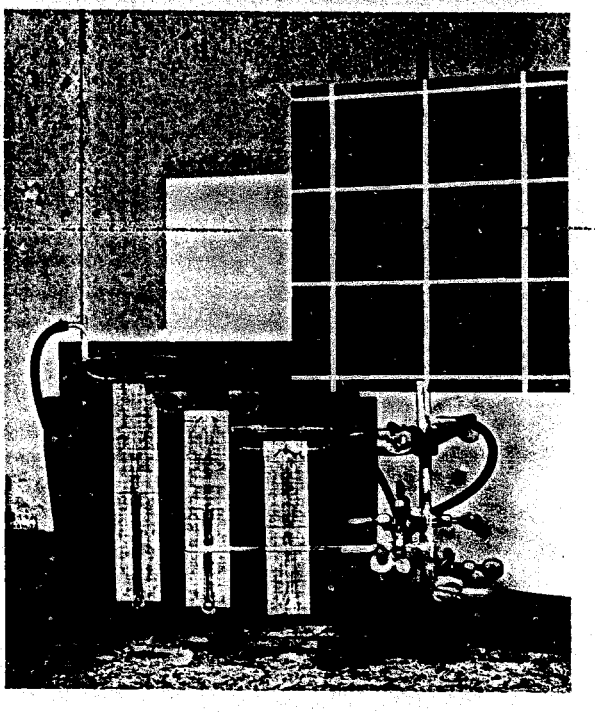

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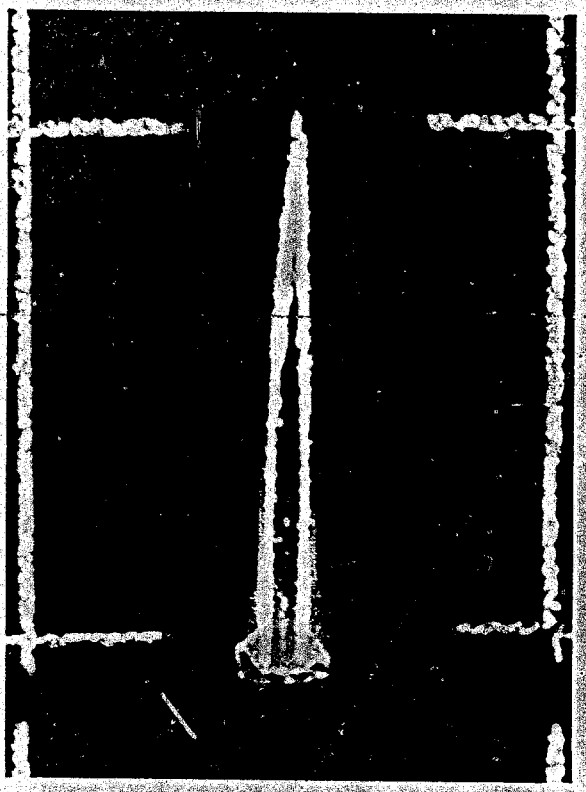


Fig. 3. Titanium particles (<44 μ) carried in an oxygen stream at 1000 cm/sec and ignited by a low, open-top pilot flame.

frames per sec were found ineffective because the particles were not bright enough to give good exposure at such high speeds. The standard procedure developed was to photograph the burning particles on color film (Anscochrome, tungsten[1]) with a 4 x 5 inch Speed Graphic[2] still camera having an Ektar f/7.7 lens[3] of 8-in. focal length with an Eastman Supermatic between-the-lens shutter.[3] Special lighting was not used. Generally a lens opening of f/11 was used to obtain sufficient field depth, but the full opening was used for particles of low luminescence. The film was specially processed to obtain a higher light speed (ASA 128) than the normal ASA 32. The subject-to-lens distance was usually about 24 in. so that the field covered was about twice the film size. A shutter speed of 1/50 sec (20 ms) was normally used and was found to be sufficiently long to record the burning of particles of concern in the experiment. The particles appeared on the film as streaks, and from these streaks the entire burning-history could be read. Burning time of the particle was taken as the duration of incandescence of the particle caused by self-heating; that is, the length of the recorded streak divided by its velocity. The particle velocity was taken as equal to the oxygen velocity at the nozzle, which in turn was found by dividing the volume rate of oxygen flow by the cross-sectional area of the nozzle; the flow rate of oxygen was monitored continuously, and a nozzle velocity of about 1000 cm/sec was generally used.

The motion pictures at normal speed (16 frames per sec) were essentially a series of still photographs because of the slow shutter-speed and the high burning

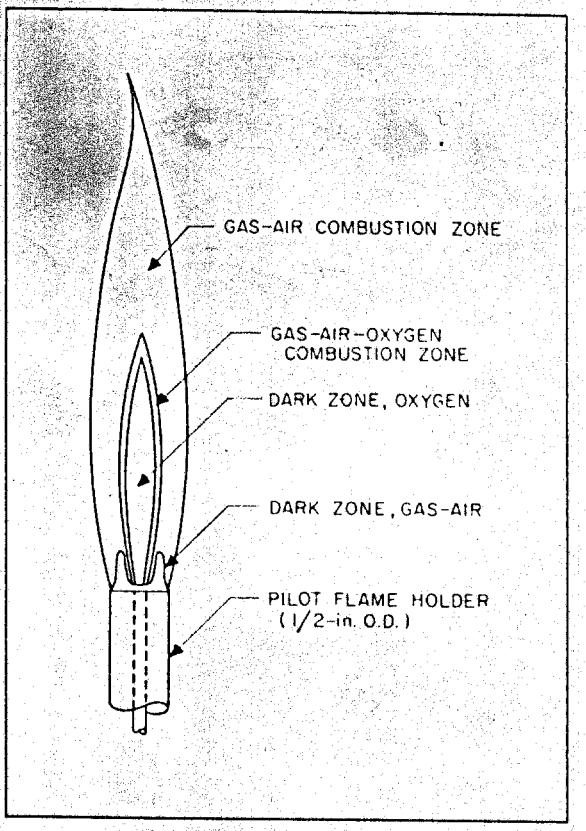


Fig. 4. Approximate appearance of a high, closed-top pilot flame for oxygen velocity of 1000 cm/sec.

[1] Manufactured by Ansco Division, General Aniline and Film Corporation, Binghamton, N. Y.
[2] Manufactured by Graflex, Inc., Rochester, N. Y.
[3] Manufactured by Eastman Kodak Co., Rochester, N. Y.

rate of the particles. Motion pictures at low speeds thus provided a convenient method of taking a large number of still photographs that provided data for statistical analysis of quantitative measurements.

Although black-and-white film with higher light speeds may be obtained, color film was used exclusively because the color of the burning particles often indicated relative temperatures and because the color of the characteristic radiation of certain elements (calcium, lithium, boron) affirmed their presence and indicated the point in time at which they were oxidized. Color film also seemed to reveal subtle differences of shade better than black-and-white film; for example, in revealing the nebulous character of the incandescent oxide cloud surrounding a burning magnesium particle. Anscochrome[1] was used in preference to other color films since it could be processed for higher light speeds without great loss of color balance. A number of photographs of burning particles are presented below but they are not faithful reproductions because of the shortcomings of black-and-white, half-tone reproduction.

C. Classification of Particle Size

For these experiments, the sizes of the particles were classified with standard screens into the following ranges: >35 mesh = >420 μ; 35-60 mesh = 420-250 μ; 60-100 mesh = 250-149 μ; 100-150 mesh = 149-105 μ; 150-325 mesh = 105-44 μ; <325 mesh = <44 μ. A closer definition of particle size was not considered necessary.

D. Substances Tested

The substances listed below were tested with the particle-burning torch. Many of the substances were of no interest as solid propellant additives, but they were tested as part of a survey to determine what mechanisms can be deduced from observation of burning characteristics and to determine the range of burning rates.

Elements: Al, B, Be, C (graphite), Co, Fe, Mg, S, Sb Si, Ti, Zn, Zr

Alloys: Al-Mg (5 to 80% Mg), AlB_2, Al-37%-Ti ($TiAl_3$), Ti-6% Al, TiB_2, MgB_2

Compounds: Al_2O_3 (for comparison), CaH_2, LiH, $LiAlH_4$, TiH_2, TiC, ZrH_2, ZrN

The above two Al-Ti alloy compositions and the compounds AlB_2 and TiB_2 represent the more prominent phases of these three alloy systems; alloys representing all the important features of the Al-Mg phase diagram were tested. In addition, two alloys, Ti-36% Al (TiAl) and Ti-23% Al, were prepared but were found to be so tough and to work-harden so much that particles for testing could not be obtained by crushing, sawing or filing. This is an example of one of the major problems encountered in obtaining unusual alloy powders.

E. Limitations of the Particle-Burning Torch

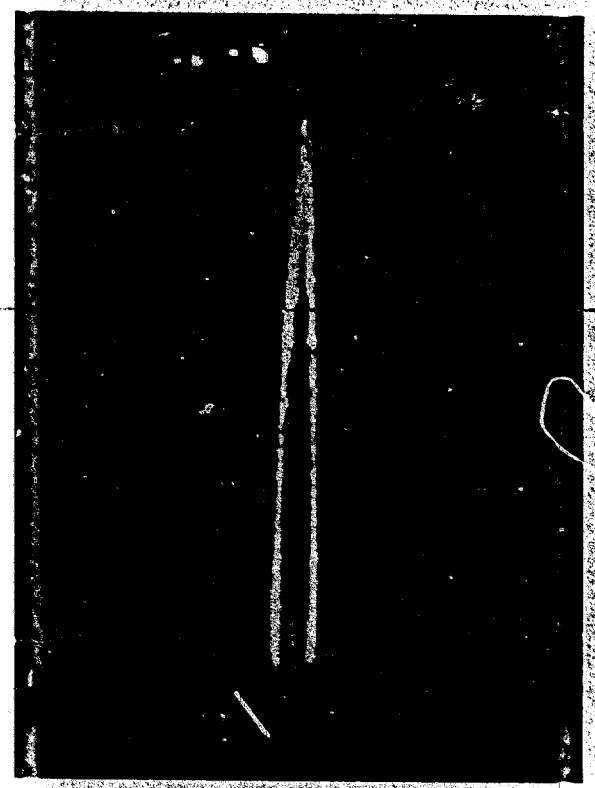
Although the particle-burning torch was intended to yield quantitative measurements of the burning rates of particles as influenced by various conditions of ignition and combustion media, the following objections to its use were found:

1. Because of turbulence and expansion of the emerging oxygen stream, the velocity of an ejected particle did not remain constant.

2. The pilot flame gave poorly defined ignition conditions. Ignition occurred at various points in the region above the torch nozzle. For example, Fig. 3 shows titanium particles (<44 μ) at 1000 cm/sec being ignited by a low, open-top pilot flame. The ignited particles formed a thin conical surface indicative of the zone in which the temperature equaled or exceeded the ignition temperature of the particles in the local composition of gas.

3. For different substances, the pilot flame had to be varied from a low, open-top flame such that the particles never passed through the combustion zone and burned in essentially pure oxygen, to a high, closed-top flame (Fig. 4) such that the particles passed entirely through the combustion zone of the pilot flame and burned in an atmosphere composed of combustion products. Hence, while the combustion of different sizes of particles of the same substance was studied under minimum ignition conditions (a procedure thought to yield the most significant information) the different sizes actually were burned in atmospheres of different compositions.

4. When a particle passes through a large pilot flame, there was a question as to which part of the streak appearing on the photographs originated from heating of the particle to incandescence by the flame and which from actual oxidation. This was particularly true when the particle photographed reached only a relatively low temperature (aluminum, beryllium, boron). There was no trouble, however, in recognizing oxidation in the instances



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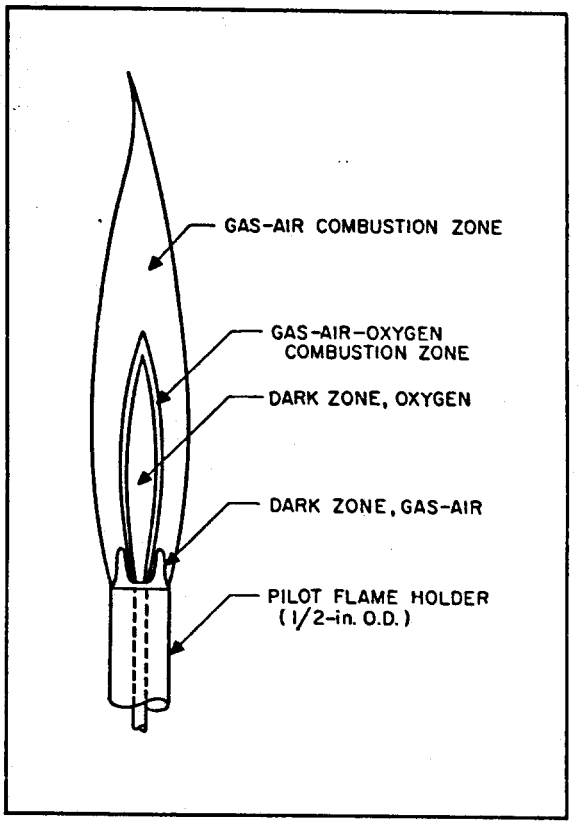

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of rapidly burning substances such as magnesium and titanium, particles of which readily achieve a bright white color. The difficulty may possibly be overcome by the addition of inert particles for comparison.

5. Some of the streaks do not represent the entire burning history of the particles because these particles may have been ignited before the camera shutter opened or they may have continued to burn after the shutter closed. This consideration is important for particles which require about 20 ms or more to burn, but it is of little consequence for fast-burning particles when numerous particles appear on the film and a meaningful average can be made. For substances with highly characteristic burning features, the beginning and the end of the burning streak can be recognized and incomplete streaks can be identified readily.

In spite of its simplicity, the particle-burning torch has been found useful in revealing large qualitative differences in the burning rates and the mechanisms of combustion which occur among certain groups of metals, and the results of the experiments have made it possible to make many observations about the nature of combustion of metal and alloy particles. These observations will help to make possible the formulation of combustible alloys with desirable properties.

F. Metallized Propellant Strands

In addition to experiments with the particle-burning torch, photographs have been made of the burning of metallized propellant strands. In these experiments, in which only a low concentration of metal particles is present, individual particles can be distinguished. A didymium glass filter is used to eliminate the characteristic yellow light which is produced by small amounts of sodium ions and which otherwise obscures many details. Metal particles within the propellant are ejected into the hot combustion gases through the steep temperature gradient which exists at a burning surface. By channeling the combustion gases through a glass tube, the metal particles are kept in contact with the hot gas and observed for a long time. This method of studying combustion of metal particles presents the advantage that ignition conditions as well as temperature and composition of the surrounding gas are well-defined and reproducible and are more closely related to actual conditions existing in rocket-motor chambers than those encountered in the particle-burning torch. On the other hand, because each particle is continuously surrounded by gas at high temperatures and is heated nearly white hot, it is more difficult in these experiments to differentiate between heat generated by the particle's combustion and heat received from contact with its surroundings than it was in experiments with the particle-burning torch. However, such characteristics as fragmentation, vaporization or serial burning (described below) may still be observed. The number of experiments carried out has been insufficient to permit complete evaluation of this method, but the tests that have been made do not contradict the conclusions based on experiments with the particle-burning torch.

III. CONCLUSIONS

A. Ignitibility

As was expected, ignitibility of a given metal – as measured by the size of pilot flame necessary to heat the particles to initiate a self-sustaining reaction – decreases with increasing particle size. Above a certain size, depending on conditions, ignition will not occur with the torch for any obtainable size of pilot flame. The surface of the particle must be heated above the temperature at which the rate of chemical reaction releases heat faster than the rate at which heat can be conducted into the center of the particle. For sufficiently large particles, the residence time in the pilot flame is not long enough to permit heating of the entire particle to the point where the rate of heat conduction from the surface is materially reduced. The upper limit of size varies for different metals; it is fairly small for aluminum and rather large for titanium. The limits tabulated in Table 2 apply only to the particular apparatus with which they were measured.

Table 2. Ignitibility limits. The diameters of the largest particles ignitible with the particle-burning torch by a pilot flame of any size.

SUBSTANCE	DIAMETER
Al	150 μ
Mg	250 μ
Ti	>420 μ
CaH_2	>420 μ
$LiAlH_4$	>420 μ

B. Burning Times

Burning times for particles of a given metal decrease with decreasing particle diameter, as was expected. The burning times of titanium and magnesium particles as a function of their diameters are plotted in Fig. 5. The quantitative data for these two metals are believed to be the most meaningful and readily comparable; in both instances particles of all sizes tested were ignited under similar conditions (by a small open-top pilot flame) and burned in atmospheres of essentially the same composition (nearly pure oxygen). The ellipses in Fig. 5 are

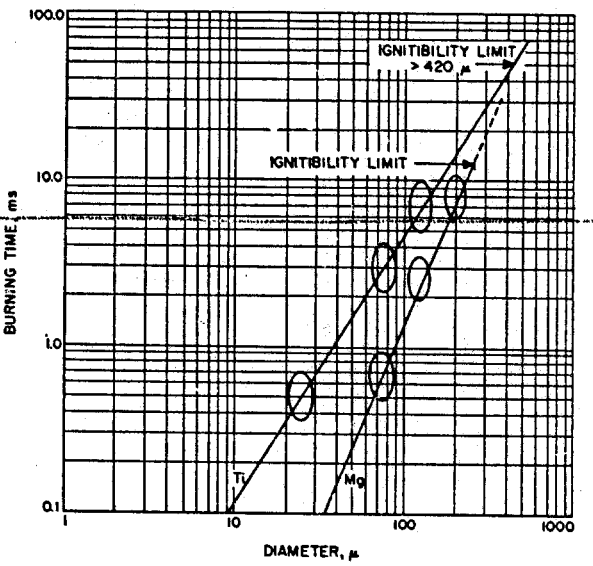

Fig. 5. Burning time vs diameter for Mg and Ti particles.

an approximate representation of the distribution of particle size and the range of observed burning times. The data are believed to be sufficiently reliable to conclude that the slopes of the straight lines are indeed different.

C. Burning Mechanisms

Particles of pure metals appear to burn according to one of five basic simple mechanisms depending, to some extent, on ignition conditions. These classifications, although greatly simplified, have been found to be highly useful and consistent in understanding the combustion of metal particles, but the possibility is not rejected that other physical processes take place and the classification may warrant further subdivision.

Class A — *Volatile metal.* The metal vaporizes at the surface of the particle and reacts with oxygen in a homogeneous gas-phase reaction. The oxide may then condense outside the reaction zone.

Class B — *Nonvolatile metal, volatile oxide.* Gaseous oxygen reacts directly with solid or liquid

metal at the surfaces of the particle; an oxide layer is not formed to impede the reaction.

Class C — *Nonvolatile metal, nonvolatile insoluble oxide.* Oxygen reacts with solid or liquid metal forming a solid or liquid oxide layer through which either oxygen or metal, or both, must then diffuse for reaction to continue. The ever-thickening oxide layer impedes the reaction to some extent regardless of whether it is porous or tightly adherent and "protective."

Class D — *Nonvolatile metal, soluble oxide.* Oxygen reacts with solid or liquid metal at the particle surface and then diffuses into the the particle away from the surface, forming a solid solution or an intermediate phase with a range of homogeneity; thus, accumulation of oxide impedes the reaction to a lesser extent than if an oxide layer were to be formed at the particle surface.

Class E — *Fragmentation.* In addition to one of the above mechanisms, a mechanism involving fracture of the particle may be imposed. Fragmentation appears to be a "catastrophe," resulting when oxidation and heat evolution take place at an ever-increasing rate, as for example: (1) when a freshly ignited magnesium particle, heated by its own diffusion flame, is able to vaporize and burn at a greater rate, or (2) when a burning titanium particle permits oxygen to dissolve more readily as it grows hotter. It is possible that fragmentation could result from internal thermal and mechanical stresses in a solid particle. Susceptibility to fragmentation could then be related to a particular crystal structure, specifically to the hexagonal structure of magnesium, titanium and zirconium, three metals which fragment readily. If, on the other hand, fragmentation takes place in a liquid droplet, then possibly it is caused by the sudden boiling of super-heated liquid.

D. Classification of Substances Tested

To which of the above classes a particular metal belongs depends to some extent on the ignition conditions. For example, under conditions normally prevailing in the particle-burning torch in which the approximate temperature range is from 500 to 1500° C, and for low particle concentrations, aluminum ($<44\ \mu$) is in class "C" (nonvolatile metal, nonvolatile insoluble oxide). However, when the concentration of metal particles in the oxygen stream is increased, the combustion of many particles raises the environmental temperature. The concentration of particles of aluminum may be increased such that the environmental temperature exceeds the boiling point of the metal, thus placing it in class "A" (volatile metal). When this happens, the mass of long streamers ejected by the particle torch collapses into a small brilliant spot of light.

The substances investigated are classified below according to burning mechanism for ignition conditions prevailing at very low particle concentration and with the smallest pilot flame capable of giving ignition. To the extent that tests have been made, the following classifications apply also for particles ejected from burning metallized propellant strands.

a. Volatile substance: CaH_2, LiH, Mg, MgH_2, S, Sb, Zn. Figures 6 and 7 are photographs of burning magnesium particles of two different size distributions. The smaller particles, Fig. 6, burned rapidly and were surrounded by an incandescent cloud of condensing magnesium oxide. The larger particles, Fig. 7, displayed the property of self propulsion and formed remarkable spiral and erratic trajectories caused by the ejection of magnesium vapor from unevenly burning particles. Magnesium hydride behaved in an identical manner. Lithium hydride and calcium hydride burned, with minor variations, in a manner similar to that shown in Fig. 6 but did not display the self-propulsion phenomenon even for particles of size 420-250 μ.

b. Nonvolatile substances, volatile oxide: B, Graphite. Isolated particles of both substances were difficult to ignite and burned slowly, appearing as sharply defined, featureless streaks having an orange color generally associated with a relatively low temperature. Boron particles were incompletely burned and became coated with oxide. Although visual evidence made it certain that a boron diffusion flame was not present, the only indication of oxide vaporization was a green tinge to the pilot flame. Boron is placed in this class because there are indications that oxide vaporization is more extensive under slightly severer conditions. Thus, massive boron crystals, heated steadily in a

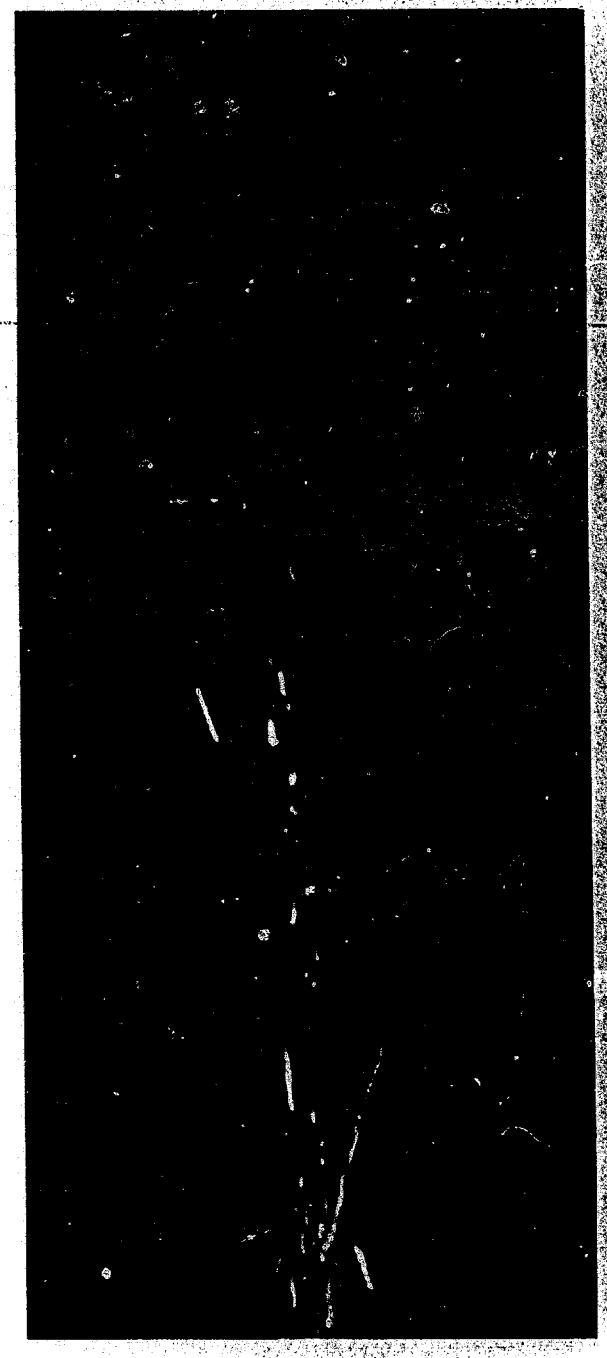

Fig. 6. Magnesium particles (105-44 μ) carried in an oxygen stream at 1000 cm/sec and ignited by a low, open-top pilot flame.

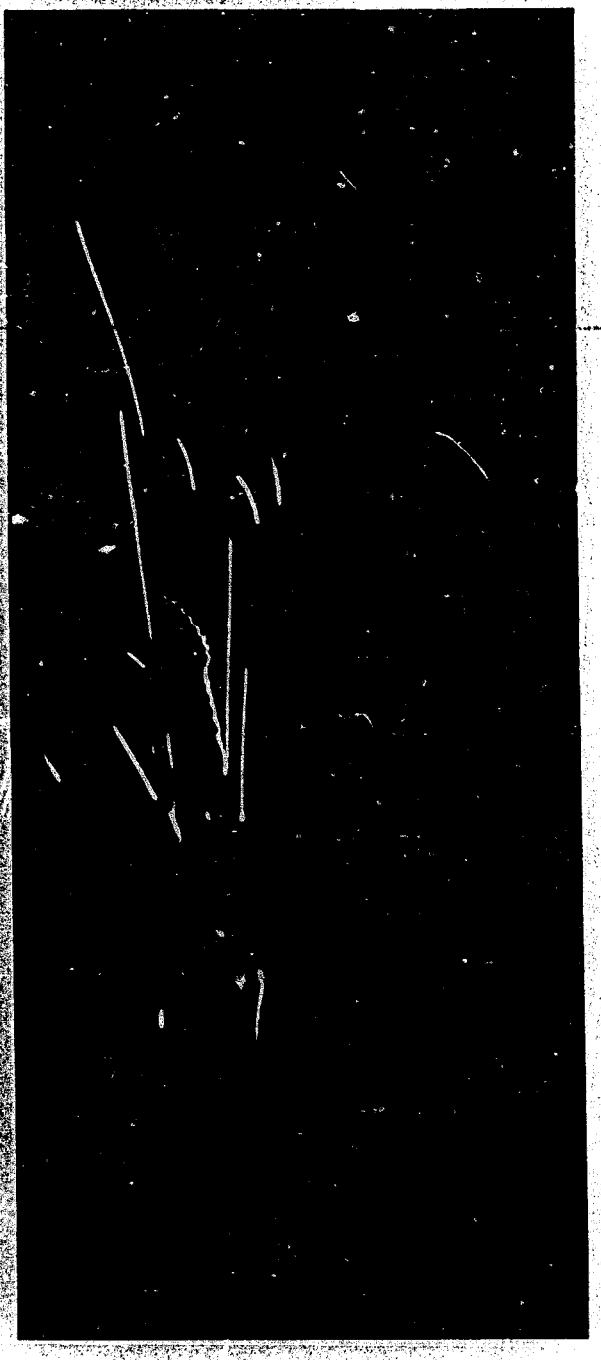

Fig. 7. Magnesium particles (250-149 μ) carried in an oxygen stream at 750 cm/sec and ignited by a high, open-top pilot flame.

metal at the surfaces of the particles an oxide layer is not formed to impede the reaction.

Class C — Nonvolatile metal, nonvolatile insoluble oxide. Oxygen reacts with solid or liquid metal forming a solid or liquid oxide layer through which either oxygen or metal, or both, must then diffuse for reaction to continue. The ever-thickening oxide layer impedes the reaction to some extent regardless of whether it is porous or tightly adherent and "protective."

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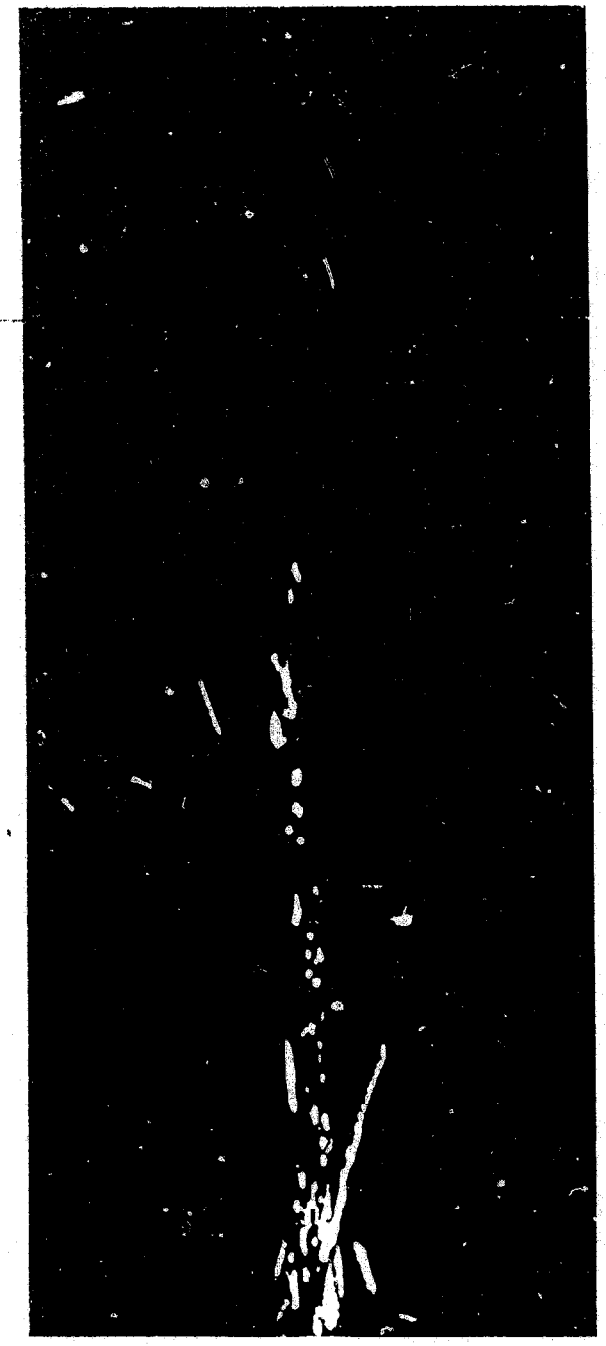

Fig. 6. Magnesium particles (105-44 μ) carried in an oxygen stream at 1000 cm/sec and ignited by a low, open-top pilot flame

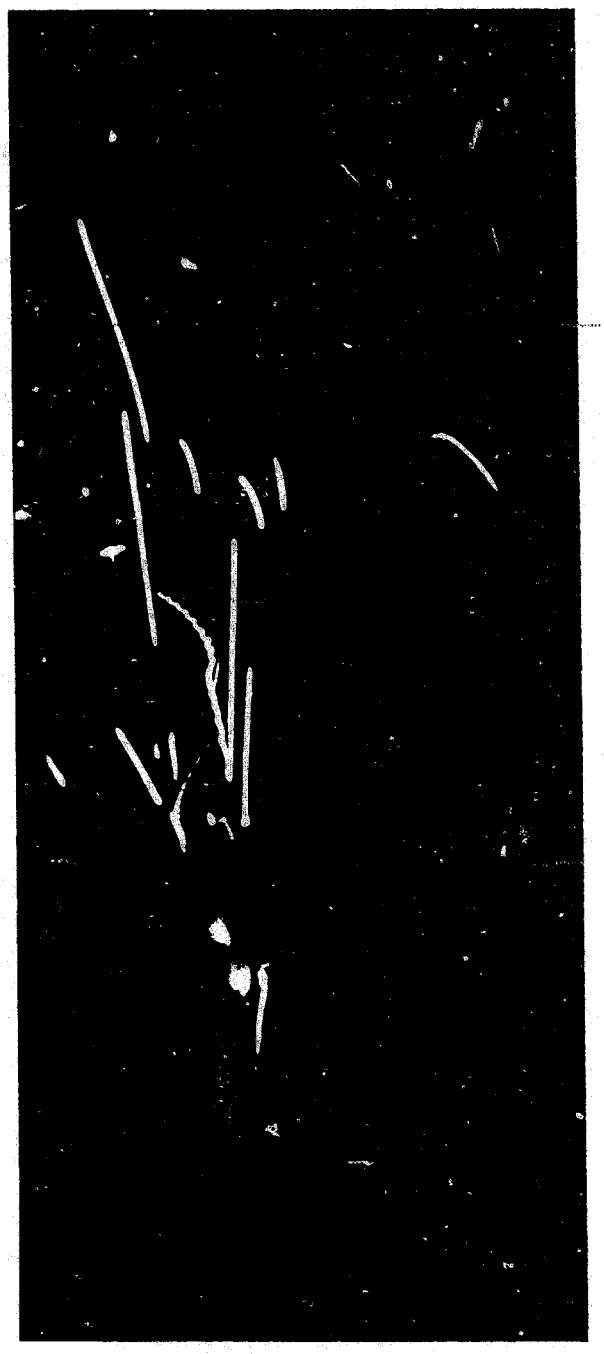

Fig. 7. Magnesium particles (250-149 μ) carried in an oxygen stream at 750 cm/sec and ignited by a high, open-top pilot flame.

gas-oxygen flame, are consumed without melting and with total vaporization of the oxide. At high particle concentration a boron-oxygen bunsen flame is readily formed. The known boiling points of carbon and its oxide place graphite in this class.

c. Nonvolatile metal, nonvolatile insoluble oxide; Al, Be, Co, Fe, Si, AlB_2, $TiAl_3$. These substances are slow burning and appear on a photograph as straight, non-fragmenting streaks which in general have a red to yellow color. Fig. 8 is typical of all the substances in this group. Of the substances tested, beryllium was perhaps the most difficult to ignite; particles were heated to a dull orange color on passing entirely through a large pilot flame and cooled rapidly outside the flame without any indication that self-heating had occurred.

d. Nonvolatile substance, soluble oxide: Ti, TiC, TiH_2, Ti-6% Al, Zr, ZrH_2, ZrN. As is well known, titanium and zirconium are capable of dissolving oxygen to form solid solutions and intermediate phases with wide homogeneity ranges (Ref. 15, 16, 17). This fact is believed to account for the unique and essentially identical burning characteristics of the substances listed. Particles are readily ignited, even for large diameters, burn smoothly for an interval, grow continuously hotter, and finally explode; these explosions give rise to characteristic star-like traces which are similar to those in the photograph of burning titanium particles in Fig. 9. The carbides, nitrides, and hydrides as well as the alloy Ti-6% Al were visually identical, but probably were slightly different in burning rates. Carbon, nitrogen, or hydrogen combined with the metal is lost during the combustion, but this process is not visible in photographs. Large quantities of alloying elements evidently interfere with the ability of titanium to dissolve oxygen, thus explaining why TiB_2 and $TiAl_3$ are in class "C."

e. Fragmentation: CaH_2, Mg, MgH_2, MgB_2, Mg-Al alloys with more than 10% Mg, Ti, TiC, TiH_2, Ti-6% Al, Zr, ZrN, ZrH_2. Figures 6, 7, 9 and 10 are photographs of burning particles in which fragmentation can be seen.

E. Serial Burning

An alloy or compound may burn by a more complex scheme than indicated above. If the alloy contains a volatile constituent (hydrogen, calcium, lithium, magnesium) as well as a nonvolatile constituent, the volatile constituent will distill out of the particle and react with oxygen in a homogeneous gas-phase reaction, leaving the nonvolatile constitutent to burn by one of the mechanisms indicated above. The distillation of a volatile component can also set up internal stresses which fracture the particle; this was observed with MgB_2 and with aluminum-

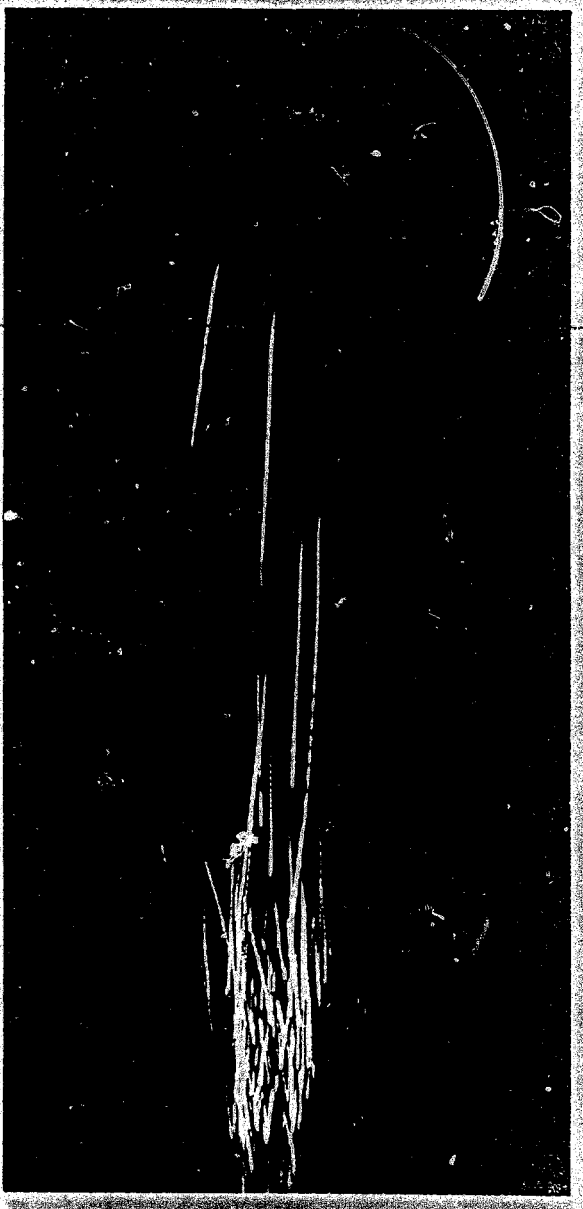

Fig. 8. Aluminum particles (105-44 μ) carried in an oxygen stream at 1000 cm/sec and ignited by a high, open-top pilot flame.

Fig. 9. Titanium particles (420-250 μ) carried in an oxygen stream at 1250 cm/sec and ignited by a low, open-top pilot flame. Shows the highly-characteristic terminal fracture.

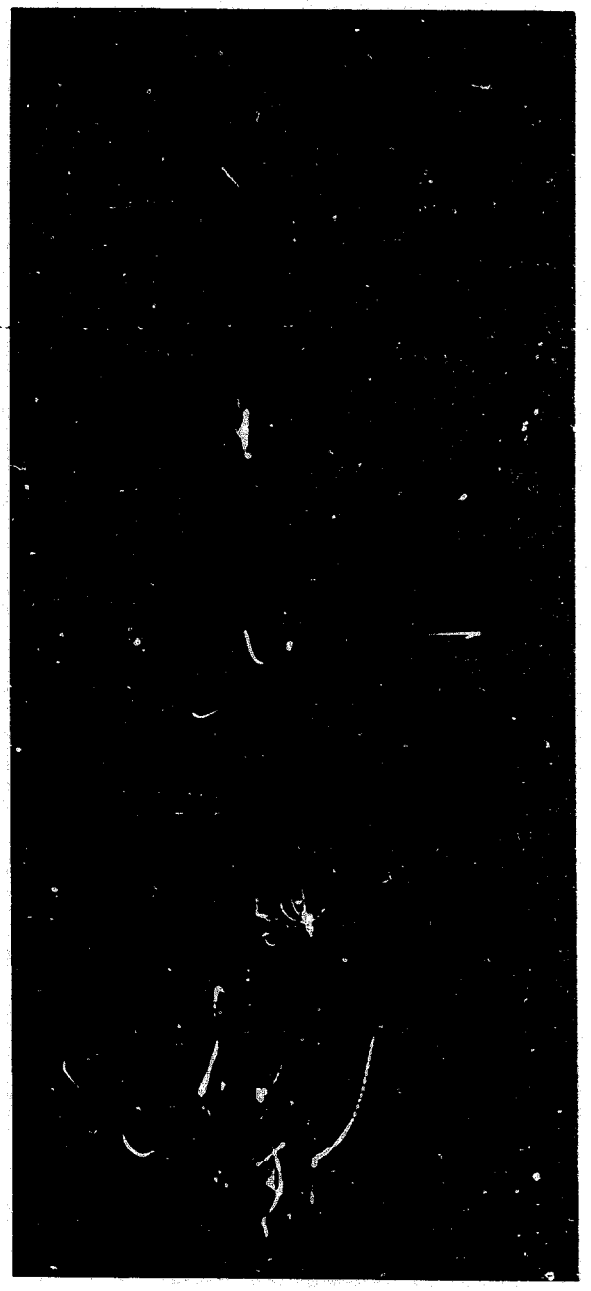

Fig. 10. Particles of aluminum-25%-magnesium alloy carried in an oxygen stream at 1000 cm/sec and ignited by an open-top pilot flame of medium height. Shows fracturing of particles and serial burning.

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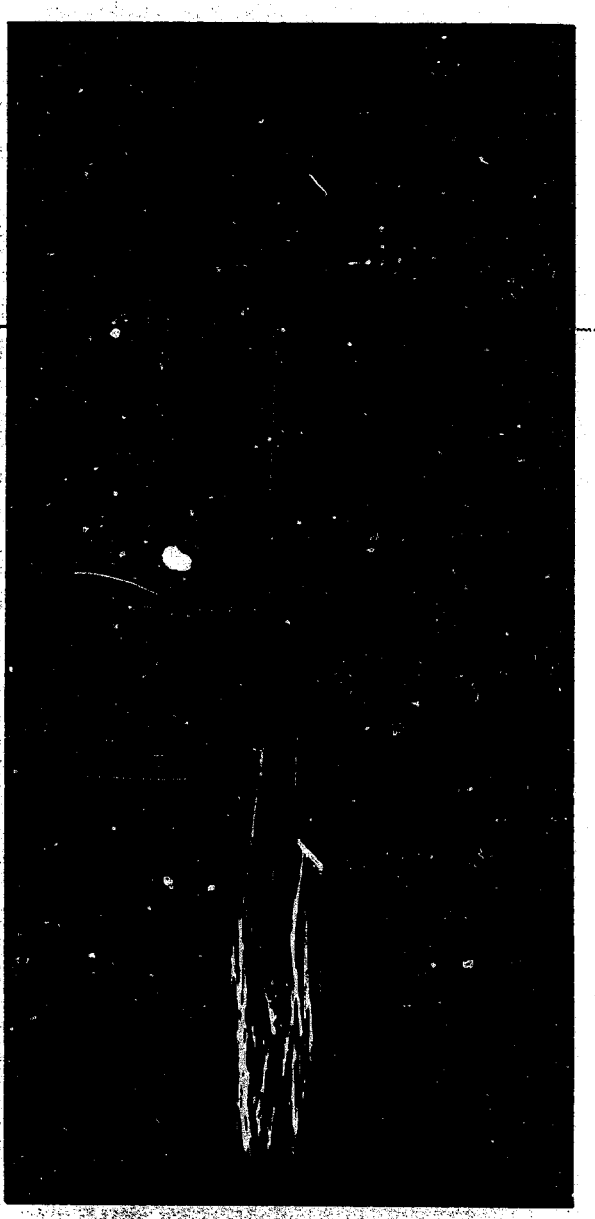


Fig. 8. Aluminum particles (105-44 μ) carried in an oxygen stream at 1000 cm/sec and ignited by a high, open-top pilot flame.

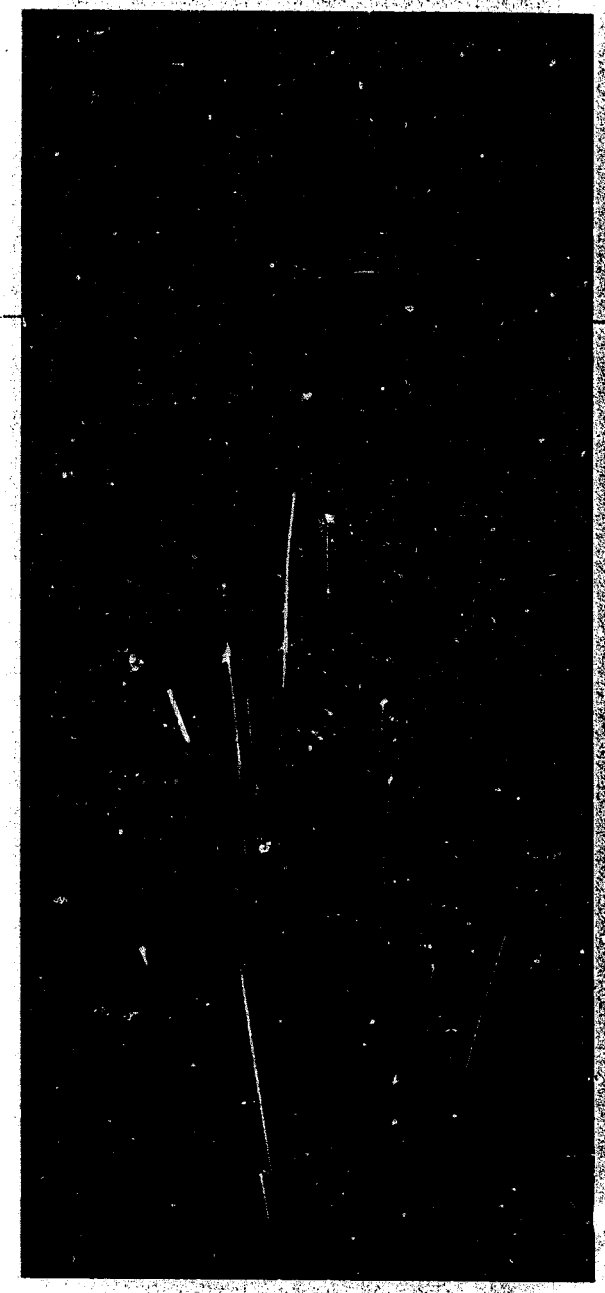
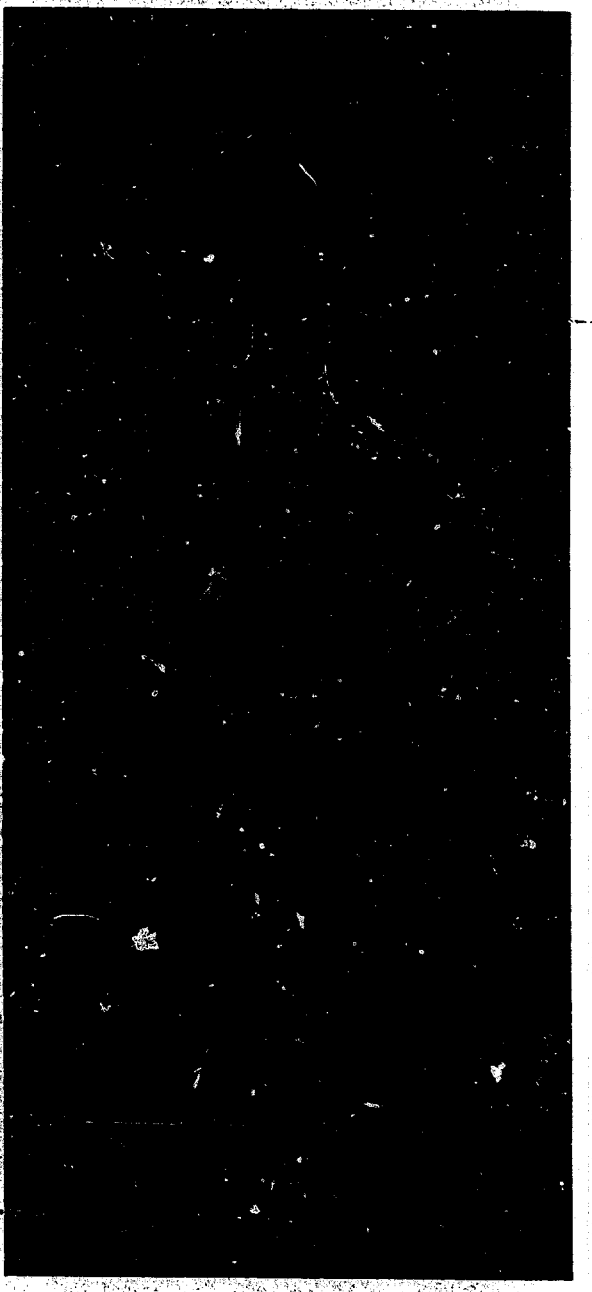


Fig. 9. Titanium particles (420-250 μ) carried in an oxygen stream at 1250 cm/sec and ignited by a low, open-top pilot flame. Shows the highly-characteristic terminal fracture.



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magnesium alloys containing more than about 10% magnesium (Fig. 10). A good example of "serial burning" according to volatility is afforded by $LiAlH_4$ (Fig. 11). When these particles burn, they appear to the eye and on color photographs as a tiny red ball surmounted by a long streak which is red and nebulous for a short distance and white and sharply defined for the remainder. From this observation, the following burning mechanism is suggested: first, all the hydrogen is released and burns instantly giving a tiny ball of flame colored red by traces of lithium; next, lithium slowly vaporizes, giving a characteristic red color to the streak; finally, the residue of aluminum continues to burn in the manner characteristic of a particle of pure aluminum. As noted above, a similar complex mechanism may be proposed for the combustion of the hydrides, carbides, and nitrides of titanium and zirconium, which are thought to burn by a mechanism involving simultaneous solution of oxygen into the metal lattice and evolution of CO_2, H_2O, or N_2.

F. Relation of Mechanical Properties to Burning Rate and Burning Mechanisms

Unlike the mechanical properties, the burning rate and burning mechanism do not appear to be sensitive to mechanical stresses, to variations in composition, or to the addition of small amounts of other elements to the metal or alloy constituting the particle. This conclusion is based on observations of burning of aluminum-magnesium and aluminum-titanium alloys and also on theoretical considerations such as the following:

1. Combustion is essentially a series of chemical reactions with rates and equilibria governed by the activities of the reactants. Small changes in concentration are expected to produce correspondingly small changes in the rate of the processes such as diffusion or vaporization which control the over-all rate of combustion.

2. Small changes in composition are also expected to make correspondingly small changes in the porosity or adhesion of an oxide layer.

3. If combustion takes place with the particle entirely liquid, then the crystal phases and residual mechanical stresses are eliminated.

Because inordinate changes in burning characteristics are not expected for small changes in the composition or manner of preparation of an alloy, it should be possible

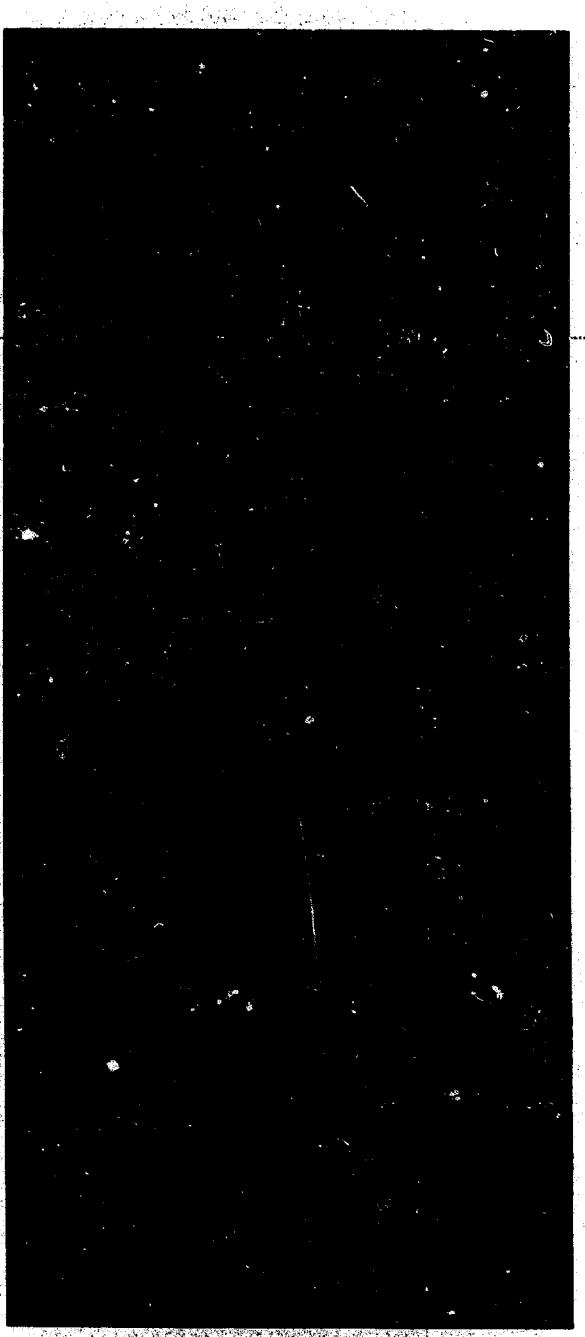

Fig. 11. Particles of lithium aluminum hydride (<149 μ) carried in an oxygen stream at 750 cm/sec and ignited by a low, open-top pilot flame. Shows serial burning.

to investigate an alloy system by studying only a few compositions corresponding to major phases of the alloy or of the mixed oxides. Further, it should be possible to confer desirable secondary properties on an alloy by modifying its composition slightly without greatly altering its burning characteristics.

G. *Relative Ignitibility*

Large qualitative differences in burning rate and ignitibility of particles of different substances for approximately the same size range were observed with the particle-burning torch. Except for magnesium and titanium, the available data do not warrant attempting to plot burning time vs. diameter. However, for particles <44 μ, Table 3 gives a qualitative classification of substances into the classes of "fast burning" and "slow burning," each substance being ignited under the minimum condition. The classifications fast and slow burning cover the approximate ranges of 0.1 to 1 ms and 1 to 10 ms respectively. Microscopic examination of particles which have passed through flames gives evidence that the slow-burning substances, particularly aluminum and boron, are incompletely burned.

In Table 4, the substances tested are classified according to relative ignitibility. All of the slow-burning substances except Fe and $LiAlH_4$ were more difficult to ignite than the fast burning substances. The substances which vaporize would be expected to be most readily ignitible and to have the highest burning rates; this was observed. Of the substances tested, those capable of dissolving oxygen (Ti, Zr. etc.) had the second highest burning rates. There is insufficient information to conclude what effect high melting point or high heat of oxidation have on ignitibility and burning rates. Aluminum-magnesium alloys are not included in Tables 3 and 4; their b ·ning rates and ignitibility ranged between that of aluminum and magnesium.

Table 3. Burning times of some substances for particles <44 microns, using in each case a pilot flame of minimum size.

FAST BURNING (< 1 ms)		SLOW BURNING (> 1 ms)	
CaH_2	TiH_2	Al	Fe
LiH	Ti-6% Al	AlB_2	$LiAlH_4$*
Mg	TiC	B	MgB_2*
MgH_2	Zr	Be	Sb
S	ZrH_2	C	Si
Ti	ZrN	Co	$TiAl_3$
	Zn		TiB_2

*The volatile contents burn rapidly, leaving a slow-burning nonvolatile particle.

Table 4. Relative ignitibility of some substances for particle of size <44 microns, as indicated by the minimum size of pilot flame necessary for ignition.

RELATIVELY EASY (Small pilot flame)		RELATIVELY DIFFICULT (Large pilot flame)
CaH_2	Sb	Al
$LiAlH_4$	Ti	AlB_2
LiH	TiC	B
Mg	TiH_2	Si
MgH_2	Zr	$TiAl_3$
MgB_2	ZrH_2	TiB_2
Fe	ZrN	

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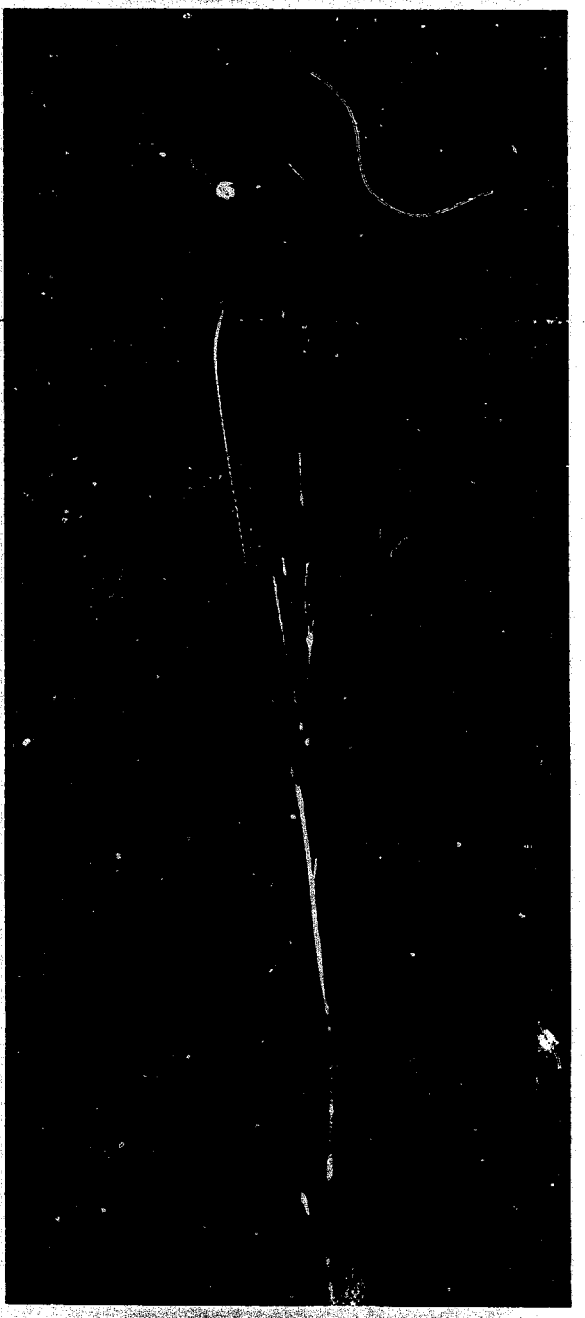

Fig. 11. Particles of lithium aluminum hydride (<149 μ) carried in an oxygen stream at 750 cm/sec and ignited by a low, open-top pilot flame. Shows serial burning.

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G. *Relative Ignitibility*

Large qualitative differences in burning rate and ignitibility of particles of different substances for approximately the same size range were observed with the particle-burning torch. Except for magnesium and titanium, the available data do not warrant attempting to plot burning time vs. diameter. However, for particles <44 μ, Table 3 gives a qualitative classification of substances into the classes of "fast burning" and "slow burning," each substance being ignited under the minimum condition. The classifications fast and slow burning cover the approximate ranges of 0.1 to 1 ms and 1 to 10 ms respectively. Microscopic examination of particles which have passed through flames gives evidence that the slow-burning substances, particularly aluminum and boron, are incompletely burned.

In Table 4, the substances tested are classified according to relative ignitibility. All of the slow-burning substances except Fe and $LiAlH_4$ were more difficult to ignite than the fast-burning substances. The substances which vaporize would be expected to be most readily ignitible and to have the highest burning rates; this was observed. Of the substances tested, those capable of dissolving oxygen (Ti, Zr, etc.) had the second highest burning rates. There is insufficient information to conclude what effect high melting point or high heat of oxidation have on ignitibility and burning rates. Aluminum-magnesium alloys are not included in Tables 3 and 4; their burning rates and ignitibility ranged between that of aluminum and magnesium.

Table 3. Burning times of some substances for particles <44 microns, using in each case a pilot flame of minimum size.

FAST BURNING (< 1 ms)		SLOW BURNING (> 1 ms)	
CaH_2	TiH_2	Al	Fe
LiH	Ti-6% Al	AlB_2	$LiAlH_4$*
Mg	TiC	B	MgB_2*
MgH_2	Zr	Be	Sb
S	ZrH_2	C	Si
Ti	ZrN	Co	$TiAl_3$
	Zn		TiB_2

*The volatile contents burn rapidly, leaving a slow-burning nonvolatile particle.

Table 4. Relative ignitibility of some substances for particle of size <44 microns, as indicated by the minimum size of pilot flame necessary for ignition.

RELATIVELY EASY (Small pilot flame)		RELATIVELY DIFFICULT (Large pilot flame)	
CaH_2	Sb	Al	
$LiAlH_4$	Ti	AlB_2	
LiH	TiC	B	
Mg	TiH_2	Si	
MgH_2	Zr	$TiAl_3$	
MgB_2	ZrH_2	TiB_2	
Fe	ZrN		

IV. DISCUSSION

When it was observed that the metals used as additives in rocket propellants (boron, aluminum and beryllium) have low burning rates and that particles of these elements retain their integrity throughout burning, the question arose as to what extent metal particles may be expected to reach chemical and thermal equilibrium with the propellant exhaust gas before reaching the nozzle throat of a rocket motor. An indirect method of determining the extent to which equilibrium is established would be to note whether the performance of a propellant approaches the theoretical performance in actual trials. On the other hand, failure to attain theoretical performance may only indicate an inaccurate calculation caused, for example, by use of inaccurate data or the failure to recognize the existence in the propellant exhaust gases of new molecular species containing the particular metal. If combustion efficiency of the metal particle is the primary factor affecting performance parameters, then experiments with an alloy of two metals which is known to have fast-burning characteristics should show it to be superior to a mere mechanical mixture of the two metals in a propellant. As has been shown, alloying can alter the burning characteristics of metals and it may be expected that by doing so the rate of attainment of thermal and chemical equilibrium also can be altered.

One of the first and more important practical results to come out of this investigation was the proposal that aluminum-magnesium alloys offer properties making them better solid propellant additives than either metal alone or in mechanical mixture. This subject is discussed at length in Ref. 18. The main advantages are:

1. Higher burning rate than aluminum.

2. Higher density than magnesium.

3. Alloys in the range 38 to 63% magnesium have a fairly protective oxide, offering propellant compatibility not shown by pure magnesium. Other compositions, except nearly pure aluminum, however, do not have a protective oxide.

4. Alloys in the range 30 to 60% magnesium are sufficiently brittle to permit pulverization by grinding, thus avoiding the more expensive, wasteful and hazardous process of atomization.

The difference in combustion characteristics of pure aluminum and of aluminum-50%-magnesium alloy considerably affect the visual burning characteristics of propellant strands. Figures 12 and 13 are photographs of burning propellant strands each weighing about 10g and containing 20% polypropylene glycol (unpolymerized), 65% ammonium perchlorate, and 15% metal particles of size $<44\ \mu$. In Fig. 12 the metal is aluminum; individual burning particles of metal can be seen. In Fig. 13 the metal is aluminum-50% magnesium alloy; here, individual particles can no longer be seen because the original particles have been disrupted to give fragments below visible size. Fragmentation not only permits the aluminum residue to burn more rapidly but also facilitates transfer of the heat of oxidation to the combustion gases of the propellant. It may be noted that the appearance of a burning strand containing pure magnesium is indistinguishable from one containing aluminum-50% magnesium alloy, while a strand containing aluminum-5% magnesium alloy is practically indistinguishable from one containing only pure aluminum. The burning rate of the alloy strand in Fig. 12 was noticeably higher than that of the aluminum strand, Fig. 13.

Beryllium has been widely considered as a performance-increasing additive. This investigation has shown that beryllium particles are difficult to ignite and slow to burn. It is therefore expected that difficulty will be encountered in trying to obtain theoretical performance with propellants containing beryllium. There is considerable room for research to improve the combustion characteristics of beryllium through alloying.

Titanium and its hydride appear interesting as additives from the standpoint of high heat of oxidation, high density, efficient burning, availability in powdered form of the desired particle size, moderate cost, and chemical inertness. However, the chemical reactions of titanium at high temperatures are complex, and thermo-dynamic performance calculations may reveal titanium to be unsuitable. Besides an ability to dissolve hydrogen and oxygen, titanium readily reacts with carbon and nitrogen and also forms volatile chlorides, and hence complicated molecular species and combustion products of titanium would be formed by reaction with the propellant gases.

Fig. 12. Burning propellant-strand (15% aluminum as particles ~ 44 μ).

IV. DISCUSSION

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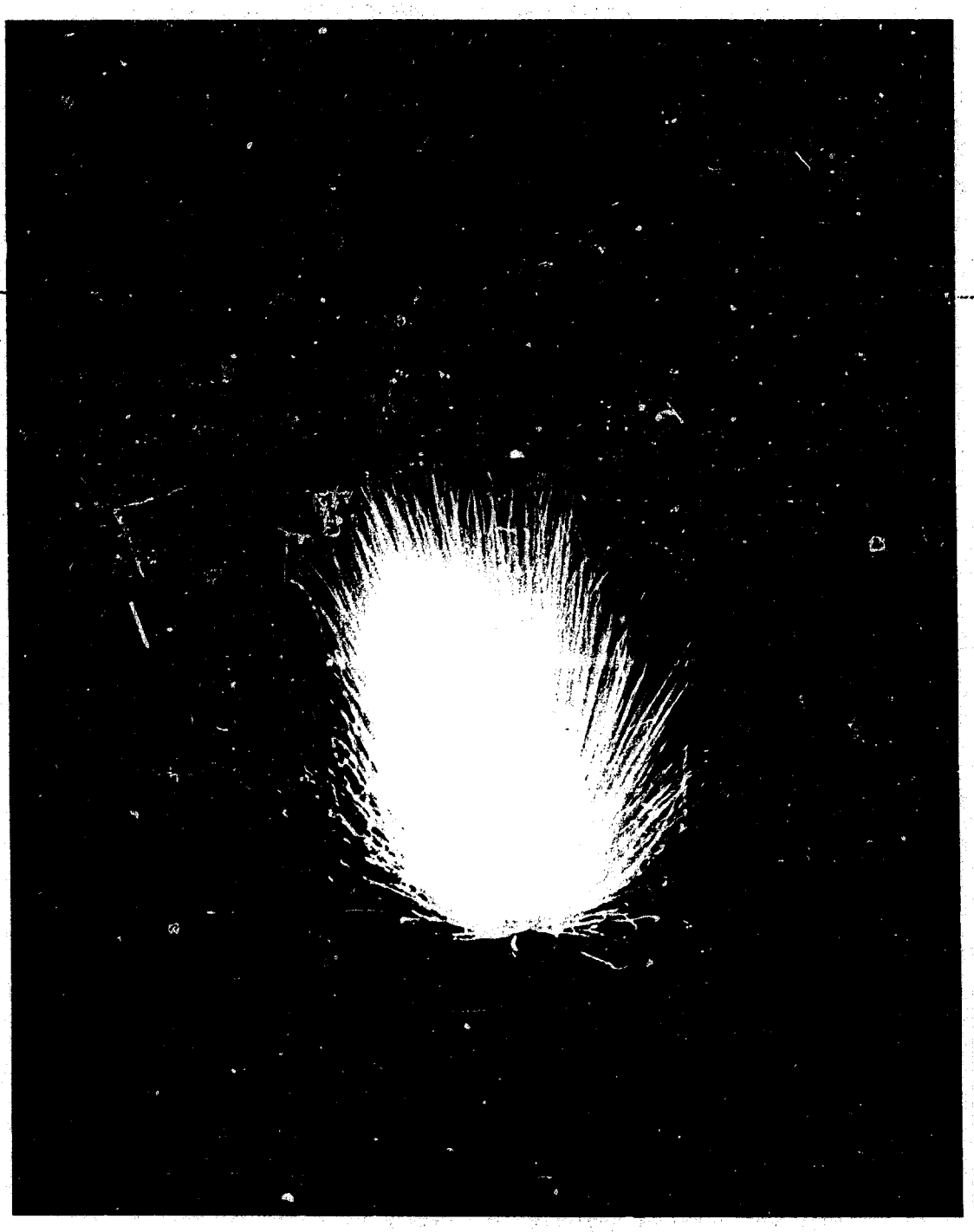

Fig. 12. Burning propellant-strand (15% aluminum as particles <44 μ).

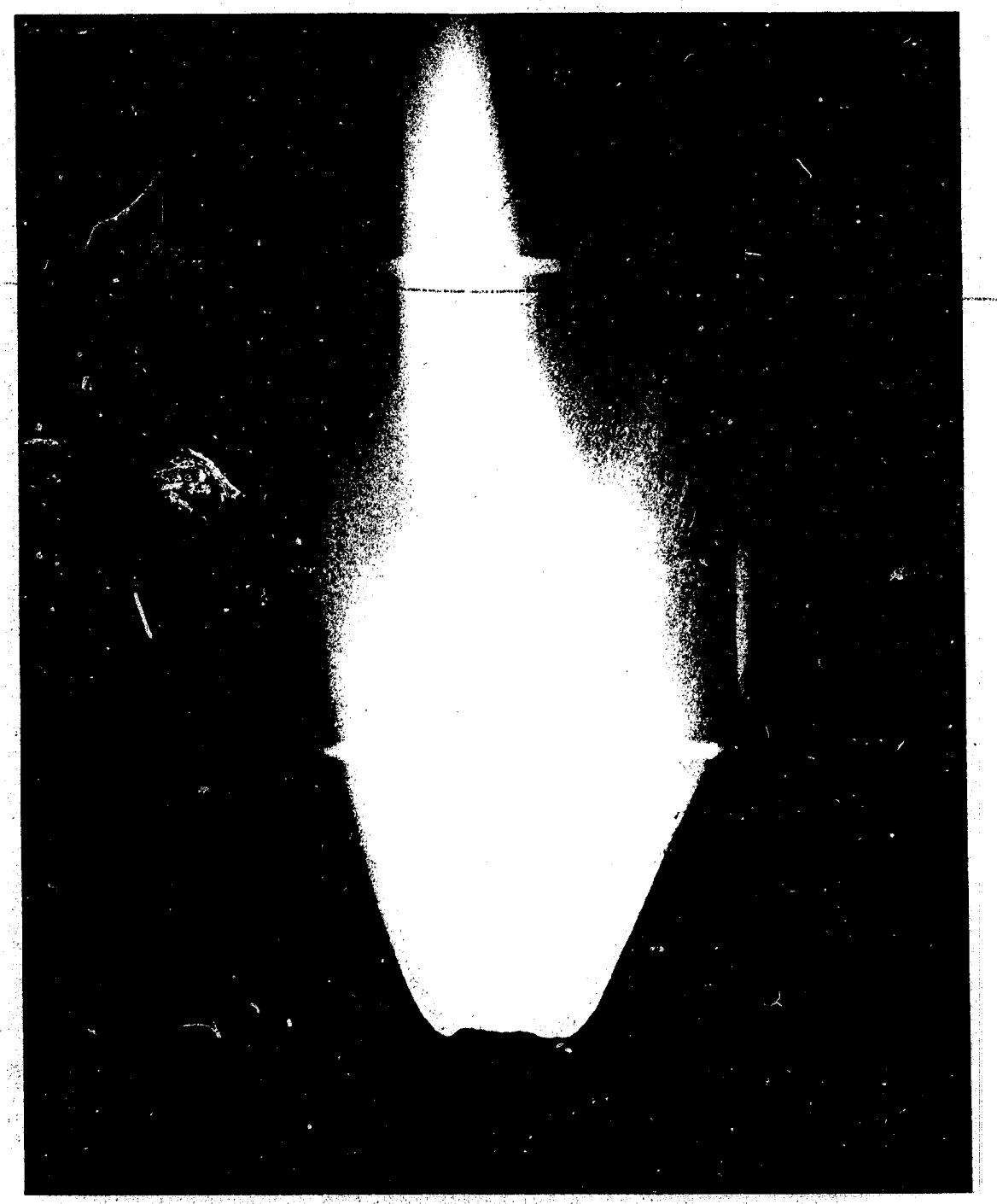

Fig. 13. Burning propellant-strand (15% aluminum-50% magnesium alloy as particles <44 μ).

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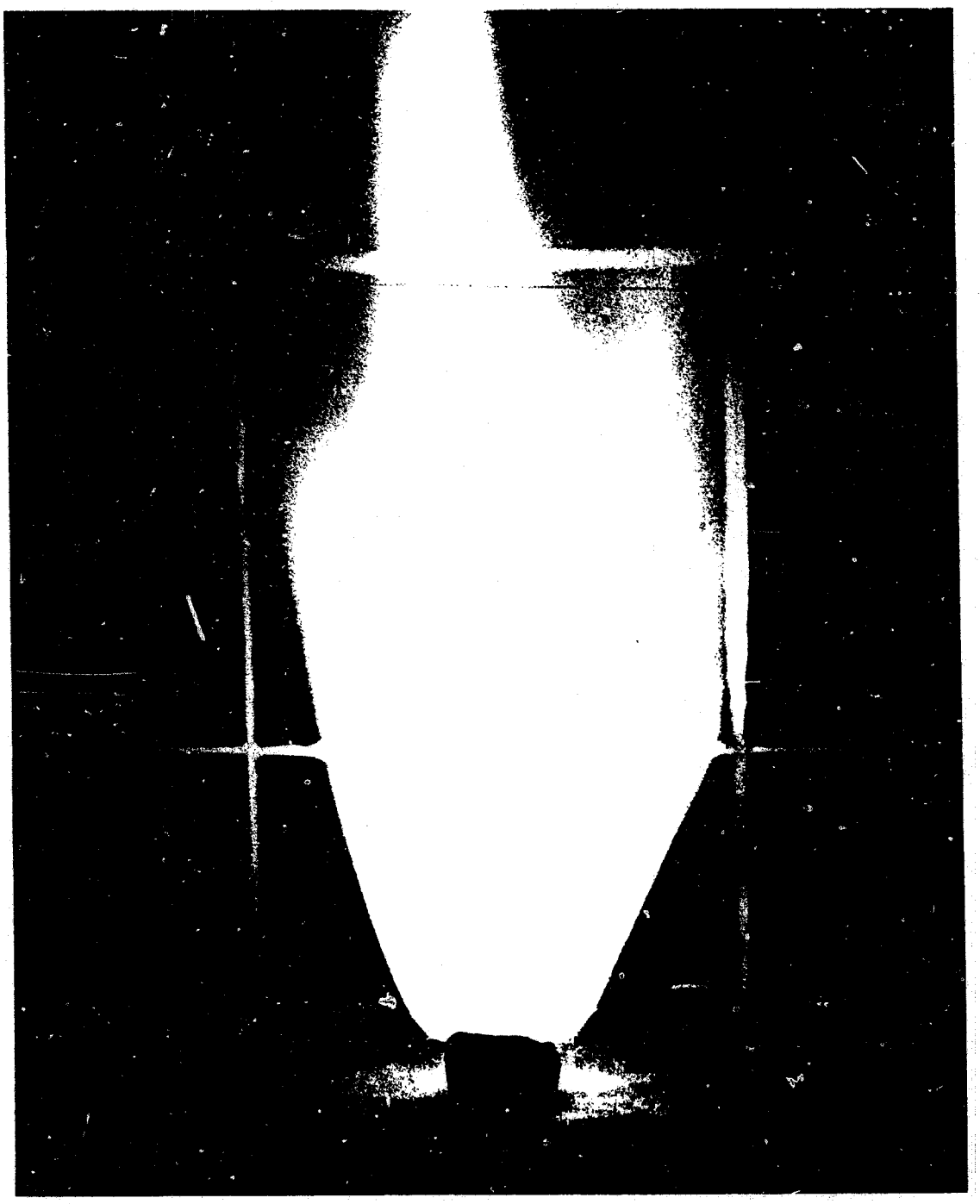

Fig. 13. Burning propellant-strand (15% aluminum-50% magnesium alloy as particles - 44 μ).

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